

**Translation**

PATENT COOPERATION TREATY

PCT/JP2003/012261



**PCT**

**INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY**  
(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>G260TJ</b>	<b>FOR FURTHER ACTION</b> See Form PCT/IPEA/416	
International application No. <b>PCT/JP2003/012261</b>	International filing date (day/month/year) <b>25 September 2003 (25.09.2003)</b>	Priority date (day/month/year) <b>30 September 2002 (30.09.2002)</b>
International Patent Classification (IPC) or national classification and IPC <b>D01F 9/14, C08L 95/00</b>		
Applicant <b>TELJIN LIMITED</b>		

<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of <u>6</u> sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> (sent to the applicant and to the International Bureau) a total of <u>5</u> sheets, as follows:</p> <p style="margin-left: 40px;"><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p style="margin-left: 40px;"><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) _____, containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>	
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the report</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input checked="" type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>	

Date of submission of the demand <b>03 March 2004 (03.03.2004)</b>	Date of completion of this report <b>07 December 2004 (07.12.2004)</b>
Name and mailing address of the IPEA/JP	Authorized officer
Facsimile No.	Telephone No.

## INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/JP2003/012261

## Box No. I Basis of the report

1. With regard to the language, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

- ☐ This report is based on translations from the original language into the following language \_\_\_\_\_, which is language of a translation furnished for the purpose of:
- ☐ international search (under Rules 12.3 and 23.1(b))
- ☐ publication of the international application (under Rule 12.4)
- ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the elements of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

- ☐ The international application as originally filed/furnished
- ☒ the description:
- pages \_\_\_\_\_ 1, 2, 4-12, 15-22 \_\_\_\_\_, as originally filed/furnished
- pages\* \_\_\_\_\_ 3, 13, 14 \_\_\_\_\_ received by this Authority on 28 October 2004 (28.10.2004)
- pages\* \_\_\_\_\_ received by this Authority on \_\_\_\_\_
- ☒ the claims:
- pages \_\_\_\_\_ 2-15, 17-29 \_\_\_\_\_, as originally filed/furnished
- pages\* \_\_\_\_\_, as amended (together with any statement) under Article 19
- pages\* \_\_\_\_\_ 1 \_\_\_\_\_ received by this Authority on 28 October 2004 (28.10.2004)
- pages\* \_\_\_\_\_ received by this Authority on \_\_\_\_\_
- ☒ the drawings:
- pages \_\_\_\_\_ 1-3 \_\_\_\_\_, as originally filed/furnished
- pages\* \_\_\_\_\_ received by this Authority on \_\_\_\_\_
- pages\* \_\_\_\_\_ received by this Authority on \_\_\_\_\_
- ☐ a sequence listing and/or any related table(s) – see Supplemental Box Relating to Sequence Listing.

3. ☒ The amendments have resulted in the cancellation of:

- ☐ the description, pages \_\_\_\_\_
- ☒ the claims, Nos. \_\_\_\_\_ 16 \_\_\_\_\_
- ☐ the drawings, sheets/figs \_\_\_\_\_
- ☐ the sequence listing (*specify*): \_\_\_\_\_
- ☐ any table(s) related to sequence listing (*specify*): \_\_\_\_\_

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- ☐ the description, pages \_\_\_\_\_
- ☐ the claims, Nos. \_\_\_\_\_
- ☐ the drawings, sheets/figs \_\_\_\_\_
- ☐ the sequence listing (*specify*): \_\_\_\_\_
- ☐ any table(s) related to sequence listing (*specify*): \_\_\_\_\_

\* If item 4 applies, some or all of those sheets may be marked "superseded."

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/JP 03/12261

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

## 1. Statement

Novelty (N)	Claims	1-15, 17-20, 27-29	YES
	Claims	21-26	NO
Inventive step (IS)	Claims	1-15, 17-20, 27-29	YES
	Claims	21-26	NO
Industrial applicability (IA)	Claims	1-15, 17-29	YES
	Claims		NO

## 2. Citations and explanations

Claims 1-15, 17-19 and 27-29

Document 1 discloses the feature of producing a carbon fiber by spinning a mixture that comprises a thermoplastic resin and a phenol resin so as to form a precursor fiber, stabilizing the precursor fiber and removing the thermoplastic resin. However, the carbon precursor indicated therein is not thermoplastic; therefore, the invention that is disclosed in document 1 differs from the invention that is set forth in claim 1. In addition, document 2 discloses the feature of producing a carbon fiber by subjecting a thermoplastic polymer and a thermoplastic precursor such as a mesophase pitch to composite spinning so as to form a precursor fiber, stabilizing the precursor fiber and removing the thermoplastic resin. However, the method indicated therein does not include the feature of spinning a mixture; therefore, the invention that is disclosed in document 2 differs from the invention that is set forth in claim 1. Consequently, the invention that is set forth in claim 1 is novel.

Furthermore, as a result of conducting a stabilizing process that employs oxygen and/or halogen gas in order to stabilize the precursor fibers, etc., and then removing the thermoplastic resin, the invention that is set forth

in claim 1 exhibits an effect whereby the thermoplastic carbon precursor does not suffer from problems related to thermal decomposition or fusion; therefore, the invention that is set forth in claim 1 involves an inventive step.

In addition, the inventions that are set forth in the claims which cite claim 1 are also novel and involve an inventive step, for the same reason.

#### Claim 20

The documents do not disclose or suggest the feature of forming a stabilized precursor overlay film, removing the thermoplastic resin from the stabilized precursor overlay film so as to form a fibrous carbon precursor mat and then subjecting the fibrous carbon precursor mat to carbonization or graphitization; therefore, the invention that is set forth in claim 20 is novel and involves an inventive step.

#### Claims 21-26

Compositions that comprise a thermoplastic resin and a thermoplastic carbon precursor such as a pitch are disclosed in documents 3 and 4. Furthermore, document 4 indicates an average particle diameter of 300 $\mu$ m or less, which includes the range of 50 $\mu$ m or less, and it is understood that said it is possible to adjust this range, as desired; therefore the inventions that are set forth in claims 21-26 lack novelty.

#### Citations:

Document 1: Asao OYA and Naoto KASAHARA, "Preparation of Thin Carbon Fibers from Phenol-formaldehyde Polymer Micro-beads Dispersed in Polyethylene Matrix," Carbon, 2000, Vol. 38, pp. 1141-1144

Document 2: JP 3-64525 A (Toyobo Co., Ltd.), 19 March

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/JP 03/12261

1991

Document 3: US 5100937 A (Nippon Oil Co., Ltd.), 31  
March 1992

Document 4: JP 62-36465 A (Unitika, Ltd.), 17 February  
1987

## INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/JP2003/012261

## Box No. VI Certain documents cited

## 1. Certain published documents (Rule 70.10)

Application No. Patent No.	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
JP 2003-336130 A (E, X)	28 November 2003 (28.11.2003)	26 June 2002 (26.06.2002)	15 March 2002 (15.03.2002)

## 2. Non-written disclosures (Rule 70.9)

Kind of non-written disclosure	Date of non-written disclosure (day/month/year)	Date of written disclosure referring to non-written disclosure (day/month/year)
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- polycarbodiimide, polyimide, polybenzazole and  
aramide into a precursor fiber or a precursor film;
- (2) 5     subjecting the precursor fiber or film to a  
stabilization treatment by contacting to gas containing  
oxygen and/or halogen gas to stabilize the  
thermoplastic carbon precursor contained in the  
precursor fiber or film so as to form a stabilized  
precursor fiber or film;
- (3) 10     removing the thermoplastic resin from the stabilized  
precursor fiber or film to form a fibrous carbon  
precursor; and
- (4)     carbonizing or graphitizing the fibrous carbon  
precursor to form a carbon fiber.

According to the present invention, secondly, the  
15   above objects and advantages of the present invention are  
attained by a process for manufacturing a carbon fiber mat,  
comprising the steps of:

- (1) 20     melt extruding a mixture of 100 parts by weight of a  
thermoplastic resin and 1 to 150 parts by weight of at  
least one thermoplastic carbon precursor selected from  
the group consisting of pitch, polyacrylonitrile,  
polycarbodiimide, polyimide, polybenzazole and  
aramide to form a precursor film;
- (2) 25     subjecting the precursor film to a stabilization  
treatment to stabilize the thermoplastic carbon  
precursor contained in the precursor film so as to form  
a stabilized precursor film;
- (3) 30     laminating together a plurality of the stabilized  
precursor films to form a stabilized precursor  
laminated film;
- (4)     removing the thermoplastic resin from the stabilized  
precursor laminated film to form a fibrous carbon  
precursor mat; and
- (5) 35     carbonizing or graphitizing the fibrous carbon  
precursor mat to form a carbon fiber mat.

According to the present invention, thirdly, the above

the precursor fiber or film is subjected to a stabilization treatment to stabilize the thermoplastic carbon precursor contained in the precursor fiber or film so as to form a stabilized precursor fiber or film.

5           The stabilization of the thermoplastic carbon precursor is a necessary step for obtaining a carbonized or graphitized fine carbon fiber. When the thermoplastic resin and the copolymer are removed without carrying out this step, the thermoplastic carbon precursor thermally decomposes or  
10 fuses. As the gas component in use for stabilization treatment, mixed gas containing oxygen and/or halogen gas is/are used from the viewpoints of permeability into the above thermoplastic resin and adsorption to the thermoplastic carbon precursor and to make the thermoplastic  
15 carbon precursor infusible quickly at a low temperature. Examples of the halogen gas include fluorine gas, chlorine gas, bromine gas and iodine gas. Out of these, bromine gas and iodine gas are particularly preferred. For infusibilization in a gas stream, the precursor fiber or film  
20 is treated in a desired gas atmosphere preferably at 50 to 350°C, more preferably at 80 to 300°C for 5 hours or less, preferably 2 hours or less. The softening point of the thermoplastic carbon precursor contained in the precursor fiber or film is sharply elevated by the above  
25 infusibilization but it is preferably 400°C or higher, more preferably 500°C or higher to obtain a desired fine carbon fiber.

          In the following step (3) of the present invention, a fibrous carbon precursor is formed by removing the  
30 thermoplastic resin from the stabilized precursor fiber or



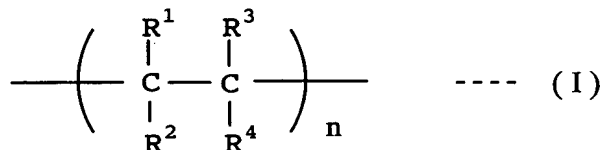
## CLAIMS

1. (amended) A process for manufacturing a carbon fiber, comprising the steps of:

- 5 (1) spinning or forming a mixture of 100 parts by weight of a thermoplastic resin and 1 to 150 parts by weight of at least one thermoplastic carbon precursor selected from the group consisting of pitch, polyacrylonitrile, polycarbodiimide, polyimide, polybenzazole and aramide into a precursor fiber or a precursor film;
- 10 (2) subjecting the precursor fiber or film to a stabilization treatment by contacting to gas containing oxygen and/or halogen gas to stabilize the thermoplastic carbon precursor contained in the precursor fiber or film so as to form a stabilized precursor fiber or film;
- 15 (3) removing the thermoplastic resin from the stabilized precursor fiber or film to form a fibrous carbon precursor; and
- 20 (4) carbonizing or graphitizing the fibrous carbon precursor to form a carbon fiber.

2. The process according to claim 1, wherein the thermoplastic resin has a free volume diameter at 20°C measured by a positron extinction method of 0.5 nm or more.

3. The process according to claim 1, wherein the thermoplastic resin is represented by the following formula (I):



30 wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are each independently a hydrogen atom, alkyl group having 1 to 15 carbon atoms, cycloalkyl group having 5 to 10 carbon atoms, aryl group having 6 to

$0.7 < (\text{surface tension of homopolymer (F)}) / (\text{surface tension of thermoplastic carbon precursor}) < 1.3$  (3)

$0.7 < (\text{surface tension of homopolymer (F)}) / (\text{surface tension of thermoplastic resin}) < 1.3$  (4).

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9. The process according to claim 8, wherein the polymer segment (e1) is a styrene homopolymer or copolymer.

10. The process according to claim 8, wherein the polymer segment (e2) is an ethylene homopolymer or copolymer.

11. The process according to claim 8, wherein the copolymer (E) is a graft copolymer or block copolymer.

12. The process according to claim 1, wherein the spinning and film formation of the step (1) are carried out by melt extrusion.

13. The process according to claim 12, wherein the melt extrusion is carried out at a temperature of 100 to 400°C.

14. The process according to claim 12, wherein the film formation is carried out by shearing at 1 to 100,000 S<sup>-1</sup>.

15. The process according to claim 1, wherein a precursor fiber having an equivalent diameter of 1 to 100 μm or a precursor film having a thickness of 0.1 to 500 μm is formed in the step (1).

16. The process according to claim 1, wherein the stabilization treatment in step (2) is carried out by contacting the precursor fiber or film to gas containing oxygen and/or halogen gas.